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Infrared spectra of methanol desorption in He stream and under evacuation on CeO_2 and ZrO_2 catalysts surface

Lei Chen, Shengping Wang [a,*]

Abstract:

Infrared spectra of methanol desorption in He stream and under evacuation on CeO_2 and ZrO_2 catalysts surface were added for the article (*RSC Adv.*, 2014, 4, 30968) as a response for the letter of Dr. F. C. Meunier (DOI: 10.1039/C4RA15157G) and to make the ascription of bands of about 1096, 1054, 1032 and 1012 cm^{-1} more convincingly. After the vacuum, bands at about 1096, 1054, 1032 and 1012 cm^{-1} still exist, which indicate these bands are ascribed to chemisorbed-methoxy.

In our work,[1] infrared spectra of methanol adsorption on ceria catalysts definitely contain the features of methanol in gas phase appearing in 1054, 1031 and 1012 cm^{-1} (Fig. 2 in ref. 1) because they are carried out during adsorption process. However, these peaks are still noted when CeO_2 or ZrO_2 samples containing preadsorbed methanol are exposed to He stream for 0.5 hour followed by half an hour evacuation to 10^{-4}~10^{-5} Pa vacuum degree in order to remove the methanol in gas phase before other adsorbates are introduced. Therefore these peaks are ascribed to chemisorbed methoxy in our paper. Here, we added infrared spectra in the condition of complete desorption of gas methanol under evacuation on CeO_2 and ZrO_2 catalysts to make the ascription of bands of 1096, 1054 1032, and 1012 cm^{-1} more clearly and convincingly. Infrared spectra of methanol desorption in He stream for 0.5 h on CeO_2 and ZrO_2 were exhibited in **Fig. 1**. Peaks at 1096 and 1012 cm^{-1} on ceria catalyst are ascribed to ν(CO) of on-top methoxy and three coordinate methoxy. Peaks around 1054 and 1032 cm^{-1} stand for bridging methoxy on CeO_2 surface.[2] On zirconium surface, features around 1162 and 1032 cm^{-1} are visible which were associated with on-top methoxy and bidentate methoxy during methanol desorption.[3]

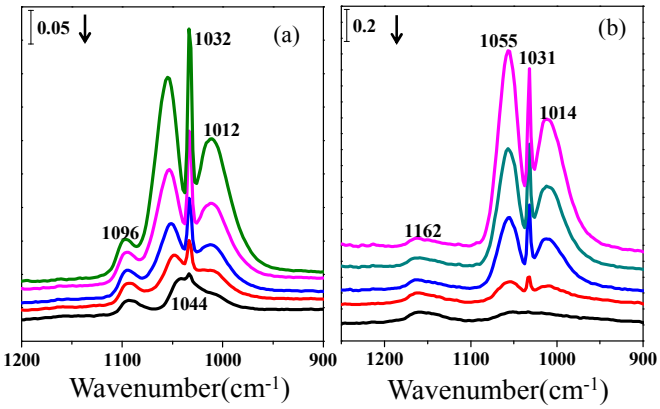

Fig. 1 Infrared spectra of catalysts containing preadsorbed methanol exposed in He stream for 0.5 h (a) CeO_2 (b) ZrO_2

To further clarify the methanol adsorption on ceria samples, Four more experiments are carried out under the same experiment conditions. **Fig. 2** exhibits infrared spectra of methanol adsorption and desorption on CaF_2 sample which is inert to methanol. As shown in Fig. 2, bands at 1057, 1033 and 1012 cm^{-1} appear when methanol is introduced. When the sample containing pre-adsorbed methanol is exposed to He stream, the bands appearing during the adsorption process all decrease and eventually disappear. So peaks at 1057, 1033 and 1012 cm^{-1} are ascribed to methanol in gas-phase, which accords with the results of Dr Meunier.

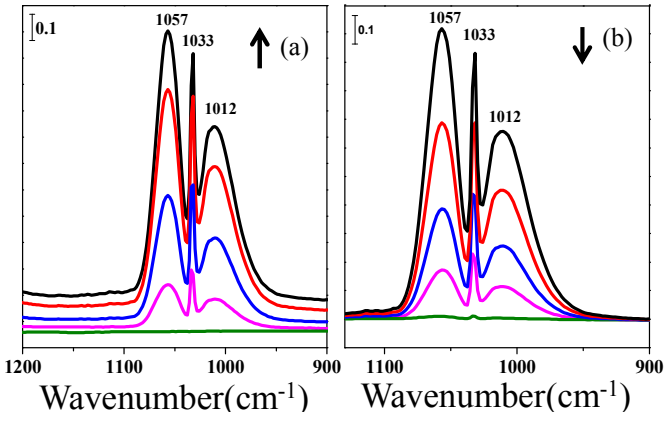

Fig. 2 Infrared spectra of methanol adsorption and desorption on CaF_2: (a) methanol adsorption (b) methanol desorption in He stream

Additionally, a mixed CeO_2 and CaF_2 sample that the weight ratio is 1:20 is exposed to methanol. Especially, He stream is followed by half an hour evacuation. The

vacuum degree during the evacuation is 10^{-4}~10^{-5} Pa. Infrared spectra are shown in **Fig. 3**. From **Fig. 3(a) (b)**, peaks at 1106, 1057, 1033 and 1012 cm^{-1} enjoy the similar tendency with that on pure ceria samples during the process of methanol adsorption and methanol desorption in He stream. Infrared spectra of sample during the evacuation are shown in **Fig. 3(c)**. Features for 1106, 1057, 1033 and 1012 cm^{-1} all decrease, but they still can be observed during the evacuation process. According to the results of CaF_2 experiment, methanol in gas-phase can be almost removed when the sample is exposed to He stream. So we prefer to ascribe these bands to the desorption of weakly chemsisorbed methoxy on ceria surface.

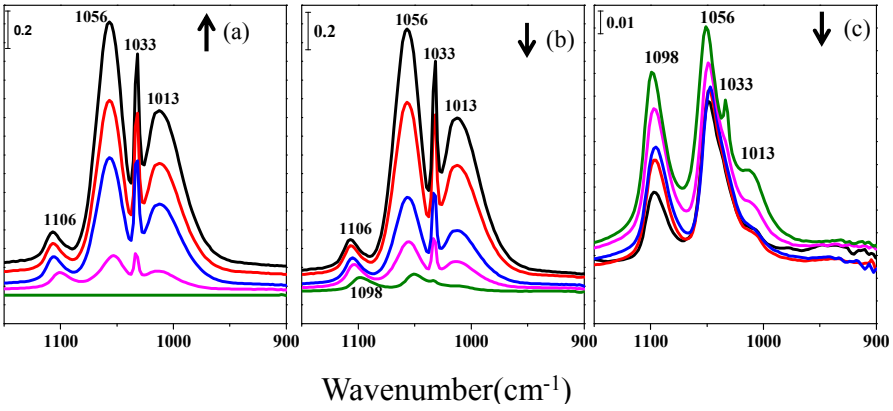

Fig. 3 Infrared spectra of methanol adsorption and desorption on mixed sample: (a) methanol adsorption (b) methanol desorption in He stream (c) methanol desorption under evacuation

Furthermore, methanol desorption from ceria and zirconium samples in He stream for 0.5 h followed by half an hour evacuation to 10^{-4}~10^{-5} Pa vacuum degree are shown in **Fig. 4** and **Fig. 5**. **Fig. 4** shows the IR spectra of methanol desorption from ceria samples. Features at 1100, 1053 and 1016 cm^{-1} which stands for ν(CO) still can be detected and attributed to on-top methoxy, bridging methoxy and three coordinate methoxy, respectively. Band around 1033 cm^{-1} may be ascribed to bridging methoxy. Features for bridging methoxy and three coordinate methoxy combine with each other along with the evacuation process. In the ν(CH_3) region there is one type of vibration: bands at 2807 and 2914 cm^{-1} are associated with the modes of ν(CH_3) and $\nu_{as}(CH_3)$ of chemisorbed methoxy. 1573, 1453 and 1370 cm^{-1} representing monodentate methyl

carbonate are weakly observed, which results from the reaction between methanol and adsorbed CO_2 on ceria. A band around 1295 cm^{-1} has been discussed in our published paper detailedly.[1] The negative-going feature around 3656 represents the OH groups decreasing during methanol adsorption.

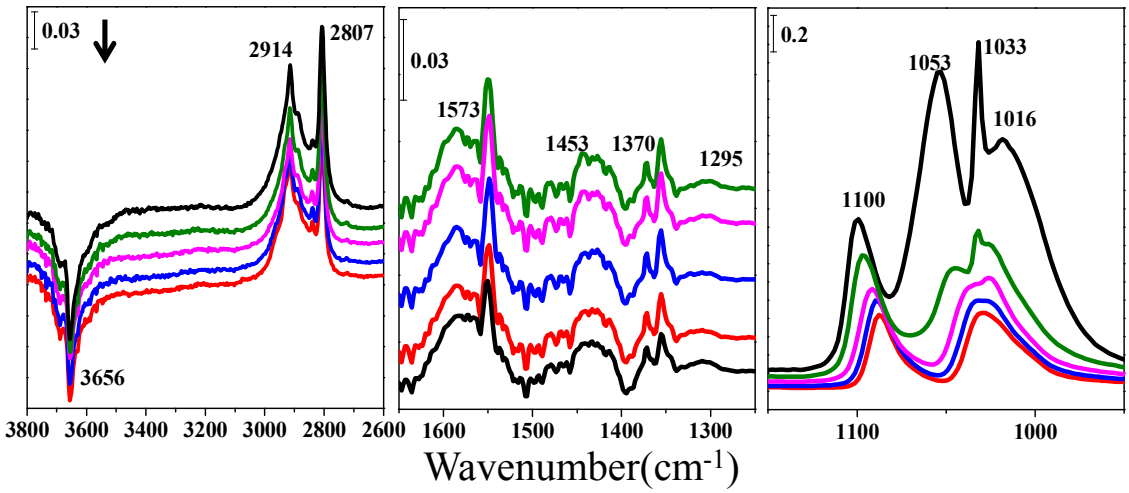

Fig. 4 Infrared spectra of methanol desorption on ceria sample

Spectra of the methanol successive desorption from zirconium sample in He stream for 0.5 h followed by half an hour evacuation to 10^{-4}~10^{-5} Pa vacuum degree are shown in **Fig. 5**. Bands at 1163 and 1033 cm^{-1} are assigned to the bending vibration of methoxy groups, while 2815 and 2920 cm^{-1} are associated with the C-H stretching vibration of bidentate and monodentate methoxy groups. Bands at 3768, 3686 and 3675 cm^{-1} are ascribed to different types of OH groups on the ZrO_2 surface. Features for 1250~1650cm^{-1} are not shown because no apparent peaks appear, indicating the absence of monodentate methyl carbonate. Compared **Fig. 5** with **Fig. 4,** chemisorbed methoxy can both be detected on these two catalysts. The difference between ceria and zirconium is the presence of monodentate methyl carbonate and the feature around 1295 cm^{-1}.

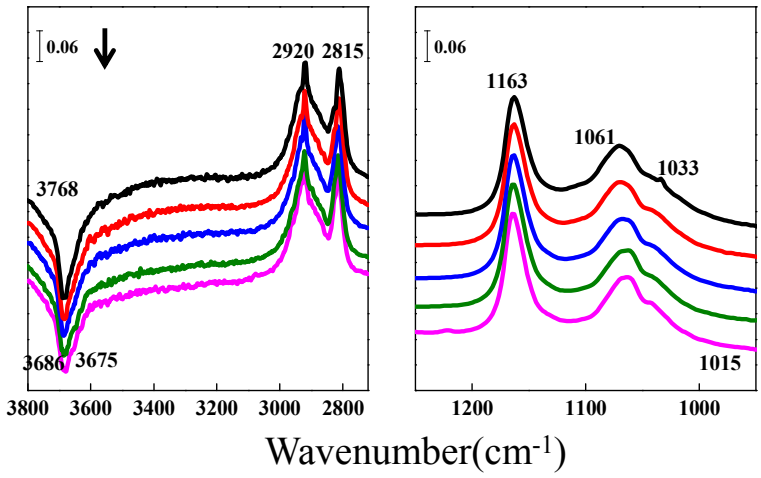

Fig. 5 Infrared spectra of methanol desorption on zirconium sample

Conclusions

Infrared spectra of methanol desorption in He stream for 0.5 h followed by half an hour evacuation to 10^{-4}~10^{-5} Pa vacuum degree on CeO_2 and ZrO_2 catalysts surface were added for the article[1] to make the ascription of bands of about 1096, 1054, 1032, and 1012 cm^{-1} more convincingly. After the vacuum, bands at about 1096, 1054, 1032, and 1012 cm^{-1} still exist, which indicate these bands are ascribed to chemisorbed-methoxy.

Notes and References

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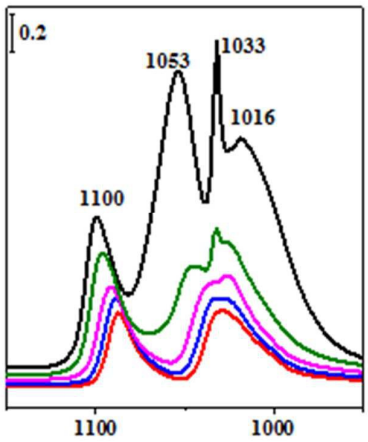
1 L. Chen, S. Wang, J. Zhou, Y. Shen, Y. Zhao and X. Ma, *RSC Adv.*, 2014, **4,** 30968-30975.

2 S. Rousseau, O. Marie, P. Bazin, M. Daturi, S. Verdier and V. Harle, *J. Am. Chem.*

Soc., 2010, **132**, 10832-10842

3 C.Binet and M. Daturi, *Catal Today*, 2001, **70**, 155-167



FTIR bands at about 1096, 1054, 1032 and 1012 cm^{-1} are ascribed to chemisorbed-methoxy on ceria.